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SOME NEW THERMOELECTRICAL AND ACTINOELECTRICAL PROPERTIES OF MOLYBDENITE.

By W. W. Coblentz.

ABSTRACT.

When molybdenite is heated by thermal conduction or exposed to thermal radiation it exhibits hitherto undescribed thermoelectric, actinoelectric, and photoelectric properties.

THERMOELECTRICAL PROPERTIES.—The first part of this paper gives data on the thermoelectric power of samples of molybdenite obtained from various localities. The observed values of thermoelectric power against copper range from about +700 microvolts through practically zero thermal emf, to −1,040 microvolts. Evidently standard thermoelectric data can not be specified.

ACTINOELECTRICAL PROPERTIES.—A new actinoelectric phenomenon is described, consisting of an emf, which is manifested in spots or loci of some samples of molybdenite, when exposed to thermal radiation of short-wave lengths. The polarity of the actinoelectric emf may be positive or negative, in spots which are separated by only 0.5 to 1.5 mm.

The spectral actinoelectric effect may be photopositive or photonegative, depending upon the wave length of the thermal radiation stimulus. The maximum actinoelectrical emf is usually produced by radiation stimuli of wave lengths between 0.65 and 0.9 μ, and no effect seems to be produced by radiation stimuli of wave length greater than 1 μ.

The time for attaining the maximum of the actinoelectric response appears to be instantaneous irrespective of the wave length of the exciting radiation.

PHOTOELECTRICAL PROPERTIES.—The photoelectrical effect (described principally in B. S. Sci. Papers Nos. 338 and 398) is manifested as a change in resistance when the molybdenite crystal is subjected to an impressed potential and exposed to light. This change in resistance may be photopositive or photonegative depending upon the wave length of the exciting radiation. The photoelectrical reaction seems to be produced by radiation of wave lengths from 0.3 to 2 μ.

The time for attaining the maximum of the photoelectrical response is a function of the wave length of the exciting radiation, requiring from one to several minutes, and twice that time for recovery after exposure. However, in the typical class of molybdenite having a low resistance, a low-photoelectrical sensitivity but a high-actinoelectrical sensitivity, the spectrophotoelectrical reaction appears to be instantaneous irrespective of the wave length.

Data are given on the effect of temperature, of the intensity of the exciting radiation, etc. In general, these factors have no marked effect upon the spectral actinoelectric reaction, or are just the reverse of the effect upon the spectrophotoelectric reaction.

When there is a close coincidence of the spots exhibiting photoelectrical and actinoelectrical sensitivity, the photoelectric current is amplified or weakened, depending upon the direction of the impressed potential through the crystals. This selective response produces a difference of 1.5 to 2.5 times between the maximum and the minimum photoelectric effect.

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I. INTRODUCTION.

Thermoelectricity is the term in common usage to designate the phenomenon that is observed when the juncture of two substances (heterogeneous circuit) is heated by thermal conduction, or by the absorption of thermal radiation as commonly observed in a thermopile. Thermoelectrical currents may be obtained also by local heating of a homogeneous (metallic) circuit consisting of a single wire which is not well annealed.[1]

[1] An interesting summary and discussion of this phenomenon is given in a paper by Foote and Harrison, Jour. Wash. Acad. Sci., 8, p. 545; 1918.

Actinoelectricity was used about 80 years ago by Hankel [2] to designate the emf generated in a crystal (for example, quartz) when connected with an electrometer or galvanometer and exposed to sunlight, daylight, or an electric arc.

A distinctive characteristic of the actinoelectric current is that it disappears immediately after obscuring the light. It is connected with the wave length (frequency) of the exciting light and not with a change in temperature, as is true of the pyroelectric current obtained in heating tourmalin.

These fine distinctions are made at the beginning of this paper in view of the fact that in the preliminary communications [3] the term *thermoelectric* was used where the term *actinoelectric* would have more accurately identified the phenomenon, which appears to depend primarily upon the wave length of the thermal radiation stimulus and not upon a temperature change in the material.

The term *photoelectric* was originally used interchangeably with *actinoelectric* to designate a direct transformation of light (thermal radiation) into electric current. In this paper the term *photoelectric* is applied to the change in resistance which a substance exhibits when it is subjected to an externally impressed emf (battery) and exposed to thermal radiation.

This paper deals with three phenomena: *Thermoelectrical*, *actinoelectrical*, and *photoelectrical*, as defined in the foregoing paragraphs.

In previous communications on this subject it was remarked that, with each renewed examination of photosensitive material in general, and of molybdenite in particular, some new and sometimes unsuspected phenomenon is observed. This in itself is an incentive to contine the work. Furthermore, the possibilities of useful applications are always present.

The subject of photoelectricity is new and the field is practically untrodden. Greater advances have been made by various investigators during the past six years in determining the general properties of photoelectrical conduction in solids by studying all sorts of material than during the preceding three decades, when investigations were confined principally to selenium. It therefore seems unfortunate that some writers who discuss [4] the recent

[2] Hankel, Abhandl. der Königl. Sächs. Gesell. der Wiss., Bd. XX; see also Wüllner's Experimental physik, 3, p. 192; 1897.

[3] Coblentz, Jour. Wash. Acad. Sci., 12, p. 411; 1922; Jour. Opt. Soc. Amer., 7, p. 63; 1923; Phys. Rev. (2 21, p. 714; 1923.

[4] For example, Pringsheim, Die Naturwissenschaften, 10, p. 335; 1922. His statement (p. 350) that the writer's measurements were made on inhomogeneous crystal conglomerates seems to be based on the fact that, in many cases, the photoelectrical reaction is localized in small spots. The use of photosensitivity as a criterion for judging the homogeneity of a crystal is novel, and if adopted would be applicable only to substances exhibiting photosensitivity.

work should question the use of natural minerals because of the uncertainty of their homogeneity and purity. Nature has had millions of years to prepare these minerals. Some of the most interesting and remarkable photoelectrical phenomena have been observed in minerals; showing what investigators may expect to attain, once they discover the secret of preparation of the material. For example, it would be interesting and useful to know how to treat the homogenous nonsensitive molybdenite so that it will exhibit the remarkable actinoelectrical properties described in this paper.

Hence, until we know some of the secrets of preparation, it seems to the writer that investigators are justified in examining everything that exhibits photosensitivity.

In carrying out this policy, through the courtesy of the Case Research Laboratory and the chemistry division of this bureau, the writer was singularly fortunate in obtaining pure artificial preparations, also natural minerals, for examination.

As already stated, the continued examination of selenium, while of very great value relative to a particular material, led nowhere in general. The recent reconnaissance, however crude and unfinished, has disclosed new information concerning the effect of impurities, crystal structure, chemical constitution, atomic weight, etc., upon photosensitivity. The time seems to be at hand to begin a real investigation of the subject.

In a previous paper [5] it was found that molybdenite, from various sources, may be classified into two groups having (1) a high specific resistance and (2) a relatively low specific resistance.

Molybdenite having a high electrical resistance is rare. Some samples cut from this material exhibit, in spots, a high photoelectrical sensitivity when subjected to an impressed emf and exposed to light. Thus far the writer has found these two properties only in certain samples of material from Yorkes Peninsula, South Australia. Upon inquiry it was found that the mine from which the present material was probably obtained has been abandoned. From this it appears that further material from this source must be sought for in museums and private collections.

The molybdenite commonly obtained in the market has a relatively low specific resistance. Furthermore, it exhibits only a low, if any, photoelectrical reaction when subjected to an impressed emf (ordinary battery, and a galvanometer, in series with the molybdenite) and exposed to light.

[5] Coblentz and Kahler, B. S. Sci. Papers, 15, p. 121, 1919 (Table 3).

While this low-resistance molybdenite does not exhibit a marked photoelectrical reaction when subjected to an impressed (battery) emf, it has the extraordinary (actinoelectric) property of generating an electric current when exposed to light, but without an impressed potential.

The object of the present paper is to describe some observations of this (actinoelectric) phenomenon, which is intimately connected with the frequency (wave length) of the radiation stimulus, and hence appears to be a direct transformation of thermal radiation into electric current. However, before this can be fully established, it will be necessary to set up some criterion for distinguishing this phenomenon from that of the thermoelectric effects observed in inhomogeneous or crystalline substances when locally heated. For this reason there is included an extensive historical summary of previous observations on the thermoelectrical properties of crystals, as well as Kelvin's theoretical deductions relating to the thermoelectrical properties of crystalline substances.

In a future communication it is hoped to give information on the absorption and evolution of heat at the points in molybdenite which exhibit the new actinoelectrical effects observed without an impressed battery. The closely adjacent loci of positive and negative actinoelectric emfs might be obtained from a thermocouple. Hence, if the phenomenon is purely thermoelectric, then, on passing an electric current through the sample, the loci, which exhibit high actinoelectrical emf's when exposed to thermal radiation, should exhibit an evolution or absorption of heat (Peltier effect) as obtains in an ordinary thermocouple, and as predicted by Kelvin on the basis of the laws of thermodynamics.

It is evident that in attempting to demonstrate a direct transformation of thermal radiation ("light") into an electric current, difficulties will be experienced in distinguishing it from thermoelectric currents of the Seebeck and of the Thomson type.

As is well known, the generation of a thermoelectric current, (as most commonly utilized in a thermocouple of two metals, for example, Bi and Ag) may be accomplished by heating the juncture of two substances by thermal conduction, as, for example, by means of a flame, or by placing the juncture in an oil bath. The thermoelectric current may be generated also by covering the juncture with a substance that absorbs thermal radiation, with a resulting rise in temperature of the juncture. If the cover (for example, lampblack) is nonselective in its ab-

sorption of radiation of all wave lengths then, using an equal energy spectrum, the heat generated in the juncture, and the resulting thermoelectric current is the same for all wave lengths, and it is proportional to the intensity of the radiation stimulus.

The direction in which the thermoelectric current flows will be independent of the wave length of the light stimulus; and it will depend only upon the composition of the two elements of the thermocouple and the thermoelectric inversion point.

In contrast with this generation of a thermoelectric current (usually at the juncture of different substances) one would expect that, using an equal energy spectrum, the direct transformation of thermal radiation into an electrical current would be found to be selective with respect to the wave length of the radiation stimulus.

If it is an optical resonance phenomenon, the direction of the current produced (the polarity), should, no doubt, depend upon the wave length of the radiation stimulus acting on the substance, and it should not be produced by an equal heating by thermal conduction.

In previous communications [6] attention was called to some remarkable actinoelectrical effects that are produced in molybdenite (MoS_2) when exposed to thermal radiation, but without an impressed potential. The phenomenon appears to be entirely different (at least in magnitude) from the emf, which is produced by the application of heat to the crystal by thermal conduction (for example, by touching the surface with a hot wire) and from the emf obtained by heating the copper-molybdenite juncture, which is the well-known thermal emf of a heterogeneous circuit. In this respect the phenomenon appears to be a direct transformation of thermal radiation into an electric current.

In this connection it is important to notice that the phenomena, to be described, are observed in different parts of the crystal, which are remote from the electrodes and hence are not ascribable to a thermal radiation effect upon the contact potential, as surmised by Sheldon and Geiger [7] from their recently described observations on argentite (Ag_2S).

These phenomena seem to become more complex with each renewed inquiry into the subject. However, sufficient data are at hand to permit summarizing some of the characteristic reactions observed when molybdenite is exposed to thermal radiation either with or without an externally impressed emf.

[6] Coblentz, B. S. Tech. News Bull. No. 61, May 11, 1922; Jour. Wash, Acad. Sci. 12, p. 411 1922; Jour. Opt. Soc. Amer., 7, p. 63 1923; Phys. Rev. (2), 21, p. 714 1923.

[7] Sheldon and Geiger, Proc. Nat. Acad. Sci., 8, p. 161; 1922.

II. HISTORICAL DATA ON THE TRANSFORMATION OF THERMAL RADIATION INTO ELECTRIC CURRENT.

During the past two or three years the writer has received inquiries for a substance that "transforms sunlight directly into electricity." The inquirers seemed to have in mind some hitherto undiscovered property of matter by virtue of which an electric current is generated spontaneously from thermal radiation, particularly of short wave lengths, such as obtain in sunlight, as distinguished [8] from the following phenomena: (1) the Seebeck type of thermoelectric current, which is generated by heating the juncture of the two metals forming a heterogeneous circuit, (2) the Thomson type of thermoelectric current, which is obtained by establishing an unsymmetrical temperature gradient by local heating of a homogeneous circuit such as, for example, a metal wire, (3) the generation of an electric current by photochemical action, as, for example, by the action of light on a cuprous oxide photochemical cell,[9] or (4) the increase in electrical current flowing through a circuit containing an impressed emf and a photosensitive substance (as, for example, selenium) which increases in electrical conductivity on exposure to light.

Experiments are on record purporting to demonstrate the direct transformation of light into electric current. However, a critical analysis of the experimental procedure shows that the light waves were absorbed, causing a heating of the juncture of two dissimilar substances or local heating of a single metal. The resulting electric current is therefore ascribable to the well-known thermoelectric current which is generated when heat is applied at the juncture of two substances (usually metals), or to the thermoelectric current which arises from applying heat locally to an inhomogeneous wire.

Ries [10] has collected and described some experiments on the direct transformation of light into electric current. He cites an experiment by Bartoli [11] which has some semblance of a direct transformation of light into electric current. In his experiments Bartoli used a wooden wheel with a rim of brightly polished silver. This silver strip was severed at one point and the ends were joined to two insulated copper brushes which completed the circuit through a sensitive galvanometer. On rotating the

[8] This is the writer's analysis of the subject. The inquirers did not concern themselves with these distinctions. Their interest was in finding a light-transformer.

[9] Case, Trans. Amer. Electrochem. Soc., 31, p. 351; 1917.

[10] Ries, Wissen und Können, Das Light in Seinen Elektr. und Mag. Wirkungen, p. 226; 1909.

[11] Bartoli, Nuovo Cimento, 6, p. 240; 1903; Beibl. Ann. der Phys., 28, p. 1169; 1904.

wheel and exposing the metal wire to sunlight an electric current was generated. On reversing the direction of rotation, the direction of the current (galvanometer deflection) was reversed. This was considered a criterion for judging the direct transformation of light into an electric current.

To the writer this appears to be merely a differential warming of the ends of the rim, which (with the wires) are merely the junctures of a thermocouple. More heat is applied (by thermal conduction) to the juncture which happens to be the "end" of the metal strip than to the "beginning" of it. Reversing the direction of rotation, and, hence, of the "beginning" and the "end" of application of heat, there ensues a differential warming of the two (junctures) ends of the silver rim. In addition to this the Thomson effect no doubt also contributes to the observed emf.

The above-mentioned observations of Hankel, on crystals, probably represent more nearly, than the Bartoli experiment, a direct conversion of thermal radiant energy into electrical energy. To say that it is a resonance phenomenon does not elucidate the question. The whole subject is too new and too unexplored to permit a final analysis.

III. HISTORICAL DATA ON THE THERMOELECTRICAL PROPERTIES OF CRYSTALS.

Under this caption are given some theoretical deductions and some experimental data on the thermoelectric properties of crystalline substances, which have a direct bearing on the new data presented in a subsequent part of this paper.

Introductory to his theoretical treatment of thermoelectric currents in linear conductors of crystalline substances, Kelvin [12] calls attention to the general characteristic of matter, that physical agencies (absorption, refraction, polarization; electrical and thermal conduction; elasticity) take place with different intensities in different directions through which they act if the substance be crystalline. Hence, as regards thermoelectric currents, it follows that a crystalline substance must have different thermoelectric powers for different directions in the crystal. Consequently two bars cut from different directions in a crystal will be thermoelectrically related to one another like different metals.

[12] Kelvin, Math. and Phys. Papers, 1, pp. 266, 324, and 467. See also Liebisch, Physikalische Krystallographie, p. 170; 1891. An interesting discussion of the volta, thermoelectric and thermionic effects is given in a recent paper by Bridgman, Phys. Rev. (2), 14, p. 306; 1919.

In the general treatment of the subject Kelvin assumed two propositions which have a special bearing on the explanation of some of the phenomena observed in the present investigation on molybdenite.

In "*Proposition I*" it is assumed that a bar is cut with its longest dimension oblique to the axis of thermoelectric symmetry and that this whole bar is kept at a uniform temperature. Under these conditions an electric current, passing lengthwise through this bar, will cause an evolution of heat on one side and an absorption of heat on the opposite side of the bar.

In "*Proposition II*" it is assumed that the ends of the bar are connected with a homogeneous conducting wire, and maintained at the same temperature. Under these conditions, if the two sides of such a bar be kept at different temperatures, an electric current will flow lengthwise through the bar. The intensity of this electric current will be a function of (1) the temperature difference between the faces, (2) the thermoelectric powers obtained from bars cut parallel and perpendicular to the isotropic axis, (3) the angle at which the longitudinal axis of the bar is cut with respect to the isotropic axis, and (4) the length and thickness of the bar.

The mathematical equation deduced shows that, for bars having the longitudinal direction parallel or perpendicular to the isotropic axis, this thermoelectric current disappears. For in this case the longitudinal axis is an axis of thermoelectric symmetry.[13]

On the other hand, keeping the bar at a uniform temperature and establishing a difference of temperature at the two ends, we have the arrangement of an ordinary thermocouple, in which, however, the thermoelectric power is a function of the angle at which the longitudinal axis of the bar is cut with respect to the isotropic axis.

These deductions seem sufficient to explain the thermoelectrical reactions observed in molybdenite which probably belongs to the hexagonal system. This mineral is usually found in warped distorted masses having no marked crystalline form.

It is conceivable that the material in the cleavage pieces of molybdenite does not lie in a uniform direction with respect to the (apparent) isotropic axis of the crystal, and, hence, with the longitudinal axis of the sample under investigation. Hence, when different parts of the crystal are heated (by conduction from being

[13] Liebisch, Physikal. Krystallog., p. 181.

in contact with a hot wire) while the ends are kept at a uniform temperature (Kelvin's Proposition II) local emf's are produced which are a function of the local crystalline configuration with respect to the main structure of the crystal.

On the other hand, when the ends are at different temperatures, a thermal emf is developed, which is a function of the angle at which the longitudinal axis of the bar is cut with respect to the axis of thermoelectric symmetry; and hence the thermoelectric power (of molybdenite) varies from sample to sample as observed.

1. BISMUTH AND ANTIMONY.

Among the earlier investigations of the thermoelectric properties of anisotropic crystals are the measurements of Svanberg,[14] on bismuth and antimony, which belong to the hexagonal system. He used rods which were cut parallel (B) and perpendicular (A) to the isotropic axis. Under these conditions, thermocouples made of bismuth (or antimony) rods, of the A and B material, had a marked thermal emf. A rod cut along another direction, or a mass of irregularly crystallized material gave a negative thermal emf when joined with A and a positive value when connected with B.

2. HEMATITE.

Bäckström [15] determined the thermoelectric powers (also the thermal and electrical conductivities) of hematite (Fe_2O_3, hexagonal system) against copper. He found a thermoelectric power of +288 mv (microvolts) for a rod cut parallel to the axis, and +314 mv for a rod cut perpendicular to the axis. Koenigsberger and Weiss[16] observed a thermoelectric power of 570 mv for a rod of iron oxide (Fe_2O_3, dimensions 10 by 3 by 3 mm) cut perpendicular to the axis. These very markedly different values, for sections cut perpendicular to the axis, are of interest in connection with the present measurements on molybdenite.

3. MISCELLANEOUS DATA ON CRYSTAL FORM AND THERMOELECTRIC PROPERTIES.

In connection with the observation of positive and negative thermoelectrical properties in molybdenite, recorded in the present paper, it is of interest to cite previous observations on other minerals,[17] belonging principally to the isometric crystal

[14] Svanberg, Öfvers. K. Vetensk.-Akad. Förhandl., **93**, 1850; Compt. Rendus, **31**, 250; 1850.
[15] Bäckström, Öfvers. K. Vetensk.-Akad. Förhandl., Stockholm, No. 8, p. 553; 1888.
[16] Koenigsburger and Weiss, Ann. der Phys., **32**, p. 16; 1911.
[17] See an extensive summary in Liebisch's Physikalische Krystallographie.

system. Hankel[18] found that octahedral crystals of cobaltite, CoAsS, gave a negative thermal emf against copper while hexahedral crystals gave a positive thermal emf. Similar observations were made also on hexahedral and octahedral crystals of iron pyrites, FeS_2. These observations were verified by Marbach;[19] also by Rose,[20] who made the additional observation that some samples of pyrites exhibited positive and negative thermal emf's in different parts of the same crystal.

Stefan[21] examined a group of hexahedral crystals of galena, PbS, and found that in some samples there were spots which exhibited a positive thermal emf, while other spots were negative, against copper. Similar properties were observed by Schrauf and Dana[22] on various minerals. They found that the majority of the pyrite crystals examined were thermoelectrically negative against copper; that the positive portions appeared often to be only thin layers, of a different nature from the mass of the crystal. Homogeneous positive crystals of pyrites were found to be of exceedingly rare occurrance.

Groth [23] investigated the thermoelectrical properties of a number of crystals of smaltite, $CoAs_2$, and found that most of them were thermoelectrically negative, while others were positive, against copper. Some crystals were negative with spots having positive emf's. An observation of especial interest in connection with the present work is that, in hexahedral crystals which were irregularly intergrown, Groth observed that some parts gave a negative thermal emf while other parts exhibited a positive emf.

In concluding this citation of historical data it is relevant to emphasize that these thermoelectric properties pertain to a heterogeneous circuit, consisting of a copper or iron wire in contact with two faces of a crystal. Usually a galvanometer was used as an indicator of the polarity. In the earlier work the copper wire was heated and brought in contact with the crystal face (Marbach) or the wires were applied to the crystal faces, and one wire was heated at a short distance from the crystal face under examination (Rose). From the foregoing summary it may be noticed that the present observations of positive and negative thermal emf's in a crystal is not entirely new. The fact it had not been observed previously in molybdenite is probably owing to the limited number of samples examined.

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[18] Hankel, Pogg. Ann., 62, p. 197; 1844.
[19] Marbach, Compt. Rend., 45, p. 705; 1857.
[20] Rose, Pogg. Ann., 142, p. 1; 1871.
[21] Stefan, Pogg. Ann., 124, p. 632; 1865.
[22] Schrauf and Dana, Amer. Jour. Sci. (3), 8, p. 255; 1875.
[23] Groth, Pogg. Ann., 152, p. 249; 1874.

IV. SOME THERMOELECTRICAL PROPERTIES IN MOLYBDENITE.

Under this caption new determinations are given of the thermoelectric power of molybdenite (MoS_2, hexagonal system).

Prior to this investigation Koenigsberger and Weiss [24] (also Gottstein [25]) determined the thermoelectric power and the Thomson heat of molybdenite. The material examined (from Okanogan County, Wash.) was a cleavage section which was cut perpendicular to the *c*-axis; the size of the sample being 2.35 by 9.7 mm. The thermoelectric power of molybdenite against iron was found to be +750 mv at 23° C. and +716 mv at 70.6° C. (Gottstein).[26] They state that the thermoelectric power did not depend upon the source of the material; but the number of localities from which the material was obtained is not mentioned.[27]

The number and the size of the samples used in previous investigations probably were small in comparison with the present work. Hence, the great variability in the electrical properties, recorded in the present paper, might escape observation.

The material used in the present investigation was in the form of cleavage pieces, split perpendicular to the *c*-axis. Some of the samples were of great length (6 cm or more) and of unusual homogeneity as judged from the smoothness of the cleavage surfaces.

The first tests were made by touching an electrically heated wire (used for constructing thermocouples [28]) to the various samples of molybdenite which had previously been investigated for photosensitivity.[29] Some samples were thermoelectrically negative against the copper electrodes to which the molybdenite was soldered; other samples gave a positive thermal emf, while an occasional sample exhibited practically no thermal emf, even when the juncture was heated to 70° C. (m. p. of Wood's alloy). This seemed very puzzling until after finding the earlier work on other crystals; also Kelvin's theoretical deductions cited on a preceding page.

1. ACTINOELECTRIC EFFECTS.

As this heater (at a temperature of 50 to 70° C.) was touched to, say, the left-hand juncture, then, in successive steps, to the intervening molybdenite, and finally arriving at the right-hand

[24] Koenigsberger and Weiss, Ann. der Phys., 32, p. 10; 1911.
[25] Gottstein, Inaug. Dissertation, Freiburg in Br.; 1913.
[26] See also a discussion of the electrical properties of variable conductors, by Koenigsberger, Jahrb. der Radioäktivität und Elektronik, 9, p. 115; 1914.
[27] Reichenheim, Inaug. Diss., Freiburg, states that the material (from Washington) contained inclusions of chlorite which caused a great variability in the specific resistance.
[28] B. S. Bul., 9, p. 16; 1911.
[29] B. S. Sci. Papers, 15, p. 121; 1919.

juncture, the galvanometer registered a strong positive (or negative) thermal emf, which gradually decreased to zero (usually midway between the junctures) and then gradually increased to a strong negative (or positive) thermal emf. On holding the heater 2 to 3 mm above the sample the long wave-length radiation emitted produced similar effects, though much smaller in magnitude, and attributable to thermal conduction.

On the other hand, on focusing the short wave-length radiation from a Nernst glower, filtered through a water cell, upon different parts of the crystal, it was found that, in some of these samples, there were spots giving high (+ or −) emf's, which were evidently caused by the action of short wave length thermal radiation, as distinguished from thermal excitation resulting from a temperature rise due to conduction of heat from a body at a higher temperature.

In some cases (sample 40IId) this actinoelectrical action was so strong that daylight incident upon the molybdenite was sufficient to throw the galvanometer deflection off the scale, whereas causing a temperature rise of 70° C. (melting a globule of Wood's alloy) produced a galvanometer deflection of only 3 mm. Experimental data on this phenomenon are given in a succeeding part of this paper. (Section V.)

2. STATISTICAL DATA.

As already mentioned, the preliminary tests of thermal emf's were made by touching the molybdenite-copper junctions by means of an electrically heated wire. For this purpose these thermocouples were connected with a d'Arsonval galvanometer. Similar tests were made on a bismuth-copper thermocouple of fine (0.1 and 0.03 mm, respectively) wires used in thermopiles.

Among the samples examined were several from the Case Research Laboratory and some of the samples previously examined for photoelectrical sensitivity; viz, Nos. 1, 2, 4, 5, 8, 9, 10, 13, 14, 15, 19, 20, 22, 28, and 33.

The results of this test (see Table 1) showed that out of 27 samples of molybdenite examined 12 had a positive thermoelectric power and 15 had a negative. In addition to this, we have to consider an unusual sample (No. 40IIb) which appears to be formed by joining, end to end, two samples of the above-described positive and negative molybdenite, and sample 40IIc which is also complex, see Table 1. Samples 40IIc and 40IId are inter-

esting in view of the fact that originally they were laterally superposed, contiguous, laminations.

The foregoing information was obtained on material from various localities (Canada, Japan, Australia, etc.), having both the high and the low resistance characteristics previously mentioned. Evidently one can not obtain exact data on the thermoelectric power of molybdenite, which is probably to be expected.

TABLE 1.—Polarity of the Thermoelectric Force of Various Samples of Molybdenite Against Copper when Heat is Applied to the Junctures; also Intervening Points.

[n. s.=nonsensitive].

Sample.	Polarity.		Photoelectric action.	Actinoelectric action.	Source.
	Left juncture.	Right juncture.			
1	+	−	Very strong	Strong	Australia.
2	−	+	Strong	Weak	Do.
4	+	−	Weak	do	Do.
5	−	+	Strong	do	Do.
8	+	−	do	do	Do.
9	−	+	do	do	Do.
10	+	−	Weak	do	Do.
13	+	−	Strong	do	Do.
14	−	+	do	do	Do.
15	−	+	do	do	Do.
19	−	+	Weak (n. s.)	do	Alaska.
20	+	−	do	do	Canada.
22	+	−	do	do	Alaska.
28	−	+	Strong	do	Australia.
33	−	+	do	do	Do.
40A	−	+	Weak (n. s.)	Strong	Canada.
40B	+	−	do		Do.
40Ia	−	+			Do.
40Ib	−	+			Do.
40IIa	+	−			Do.
40IIb	− +	−	Weak (n. s.)	Strong	Do.
40IIc	− +	− +	do	do	Do.
40IId	−	+	do	Very strong	Do.
50	+	−	do	Strong	Japan.
80	+	−	do	do	Do.
80A	+	−	do	do	Do.
80B	+	−	do	do	Do.
80C	+	−	do	do	Do.
Case	+	−	do	Weak	Do.

3. THERMOELECTRIC POWER OF SELECTED SAMPLES.

It seems misleading to compile extensive data on the thermoelectric power of molybdenite. It will, therefore, suffice to give measurements on a few typical examples of the material, giving positive and negative thermal emf's.

In this paper the thermoelectric power is taken positive when the current flows in the molybdenite from the hot junction to the cold junction (see Smithsonian Phys. Tables).

In order to determine the thermoelectric power, fine (No. 38, $t=0.1$ mm) copper wires were soldered, by means of Wood's alloy,

to the ends of the samples of molybdenite. Sample No. 40IIb, had a third wire attached at the center in order to determine the thermoelectric power (positive and negative) of the two components.

The thermal emf's were measured with a potentiometer. In the samples which exhibited very low emf's the thermal emf's were determined also by connecting a copper-constantan thermocouple (of fine, No. 40 wire) in series with the copper-molybdenite thermocouple and noting the galvanometer deflections when these thermocouples were (separately) heated to 70° C. (melting point of the Wood's alloy used).

In the samples exhibiting a high thermal emf, one end of the copper-constantan thermocouple was soldered to the "hot" end of the molybdenite thermocouple. The other end of the copper constantan thermocouple was electrically insulated and placed in contact with the "cold" end of the molybdenite-copper thermocouple.

The heating device consisted of a thermally insulated vessel of hot water, to the bottom of which was attached a short block of copper, having a flat surface 5 by 10 mm in cross section. By placing this block of copper on the molybdenite-copper junction, and regulating the temperature of the water, a temperature difference of 2 to 5° C. was established between the two ends of the constantan-copper (and the molybdenite-copper) thermocouples. The ratio of the emf's of the two thermocouples gave the thermoelectric power of molybdenite-copper. Other minor experimental details need not be mentioned, except that daylight was excluded from the material, in view of its high actinoelectric power, which was very marked in sample No. 40IId.

The measurements of thermoelectric power (also the lengths between the electrodes, etc.) of various samples of molybdenite against copper are given in Table 2. They range from +700 mv (microvolts) per degree to over −1,000 mv.

Attention may be directed to sample 40IIb, which appears to be an intergrowth of the + and − material composing samples 40Ib and 40IIa, although to the eye the sample appears smooth and continuous. The general outline of this interesting crystal, No. 40, is sketched to scale in Figure 5, in which the letters, b, c, d, indicate the regions from which the samples 40I, 40IIb, etc., were cut.

TABLE 2.—Thermoelectric Power of Molybenite, MoS_2 (against Copper) in microvolts (mv) per degree. Mean Temperature of Junctions 28 to 29° C.

Sample.	Thermoelectric power in microvolts.	Size.			Source.
		Length.	Width.	Thickness.	
		mm	mm	mm	
40A	+465	27	4.5	0.12	Renfrew Co. Canada.
40B	−120	28	4.5	.05	Do.
40Ib	+690	25	3	.15	Do.
40IIa	−655	20	5	.11	Do.
40IIb	−1,040 +510	23	5	.13	Do.
40IId	+100	22	5	.15	Do.
50	−180	25	4	.16	Hida, Japan.
80A	−850	24	4	.15	Do.
80B	−860	45	3	.18	Do.

No smooth lamina could be split along the line of intergrowth, which was not sharply defined. Sample 40IIb was cut at a considerable distance from the line of intergrowth. Nevertheless it exhibited the remarkable positive and negative thermoelectrical properties just described. It is not unlike a compound thermoelectric series of copper-iron-bismuth-copper.

V. SOME ACTINOELECTRICAL PROPERTIES OF MOLYBDENITE.

In a previous paper a new negative photoelectrical reaction was described.[30] When samples of molybdenite, having this property, are connected with an electric battery and exposed to certain wave lengths of light (blue, green, and yellow), the electrical resistance is higher than when the sample is kept in the dark.

At the time when this phenomenon was observed, tests were made to determine whether the molybdenite generated an electric current when exposed to light, without an impressed potential, and it was found that, if there is such a generation of electric current (whether thermoelectric or what might be called a "spontaneous" current), it was too small to affect the measurements of the above-mentioned photonegative reaction.

The investigations to be described under this caption were begun [31] about a year and a half ago, when T. W. Case raised the opportune and interesting question whether the above-mentioned photonegative reaction is caused by an electric current, saying he had found that molybdenite is light active; that is, generates an electric current without an impressed potential. His method of

[30] B. S. Sci. Papers, No. 398, 16, p. 596; 1920.

[31] The first results were described in B. S. Technical News Bulletin No. 61, May 10, 1922.

making the test was to explore the illuminated surface (which is sensitive in spots) by touching it with fine platinum-wire electrodes, which were connected in series with a galvanometer or a photophone. Since the thermoelectric power of molybdenite is very high, the question arises whether, by this method of making the test, some of the action is thermoelectric at the contact of the two substances.

In view of Mr. Case's query, the photonegative action in molybdenite was reinvestigated. It was found, when using a very sensitive galvanometer, that, in some samples, a small electric current is generated, without an impressed potential, but it is too small to affect the photoelectrical reactions previously observed. This is owing to the fact that the samples of molybdenite which exhibit a photoelectrical reaction (resistance change when subjected to an emf and exposed to light) do not show a marked actinoelectrical reaction.

1. EXPERIMENTAL PROCEDURE.

In the present investigation the spectral measurements were made with a lens spectrometer and also a mirror spectrometer. The source of light was a 500-watt gas-filled tungsten lamp, calibrated to emit an equal energy spectrum, as described in previous papers on this subject.

For exploring the actinoelectrical reaction in different parts of a crystal an image of a ribbon-filament tungsten lamp (from the Nela Research Laboratory) was projected upon a diaphragm having a vertical slit 0.2 mm wide (1 cm long). The sample under examination was mounted upon a sliding carriage (having a graduated scale for making accurate settings) which was moved horizontally close back of this slit. In this manner the crystal could be exposed at every 0.1 or 0.2 mm along its whole length.

For exploring a light-sensitive spot more thoroughly, the carriage was held stationary back of the vertical slit, and a second horizontal slit 0.2 mm wide (1 cm long) was raised or lowered vertically on a graduated sliding carriage. In this manner the crystal could be examined widthwise, and thus the whole surface could be explored in areas 0.2 by 0.2 mm. The actinoelectric effect usually being small, the preliminary exploration of the sample was made by connecting it in series with a sensitive ironclad Thomson galvanometer.

For making the photoelectrical and the actinoelectrical tests the sample was connected with a d'Arsonval galvanometer; with and

without a dry battery in series. It is to be noted that when the battery was connected (current direct "*C. D.*," or current reversed "*C. R.*"), in series with the sample, the galvanometer deflection which is obtained on exposure of the photosensitive spot to light is the algebraic sum of the photoelectrical and the actinoelectrical reactions. The true magnitude of the photoelectrical reaction is obtained by noting the (positive or negative) galvanometer deflection caused by the actinoelectrical reaction, which is observed without the impressed battery.

The intensities of the radiation stimuli, E = 1, E = 7, etc., indicated in the illustrations are for the mirror spectrometer. The intensities used in the lens spectrometer were considerably higher, permitting observations into the violet end of the spectrum.

2. TOTAL RADIATION MEASUREMENTS.

Under this caption are given the actinoelectrical reactions of various samples of molybdenite when small areas were exposed to the total radiation of a ribbon-filament tungsten lamp. In the illustrations, the abscissas are positions along the length of the crystal, and the ordinates are the resulting galvanometer deflections when successive small portions of the crystal are exposed to radiation.

(a) ACTINOELECTRICAL SENSITIVITY OF DIFFERENT PARTS OF A LAMINA.

The actinoelectrical sensitivity in molybdenite occurs in spots as was previously found for the photoelectrical sensitivity.

Sample No. 1.—Molbydenite sample No. 1 is remarkable for its high photoelectrical sensitivity (both positive and negative), which has been subjected to numerous investigations previously described.[32] Its actinoelectrical reactions are depicted in Figure 1, from which it may be noted that the (negative) actinosensitivity extends over practically the whole length of the lamina. But there are no sharp positive and negative maxima, such as are observed in Figure 2.

This sample was very thin, and the large + and − deflections at the ends are no doubt owing to the emf's developed by heating of the molybdenite-copper junctions. This was verified by heating the junctures by thermal conduction as described under Section IV.

Samples Nos. 80, 80A, and 80C.—These samples were split from a large crystal. Although the whole length of each sample

[32] B. S. Sci. Papers, Nos. 338 and 398.

was tested, only that part which exhibited any actinoelectrical sensitivity is depicted in these illustrations. (See figs. 1 and 2.)

The actinoelectrical sensitivity of molybdenite sample No. 80 is confined to two spots (+ and −) separated by only 0.6 mm.

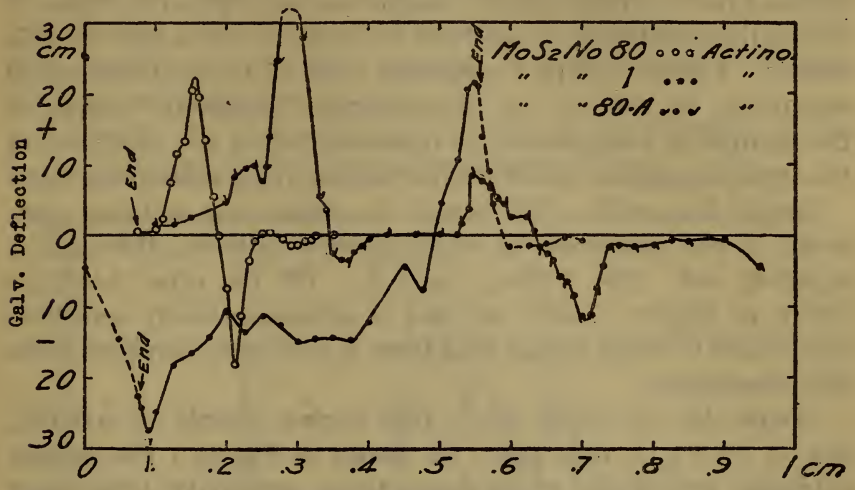

FIG. 1.—*Actinoelectric sensitivity of different parts of a lamina of molybdenite.*

Similarly in No. 80C the actinoelectrical reaction is confined practically to one narrow region of positive emf and an intense complex spot of negative emf.

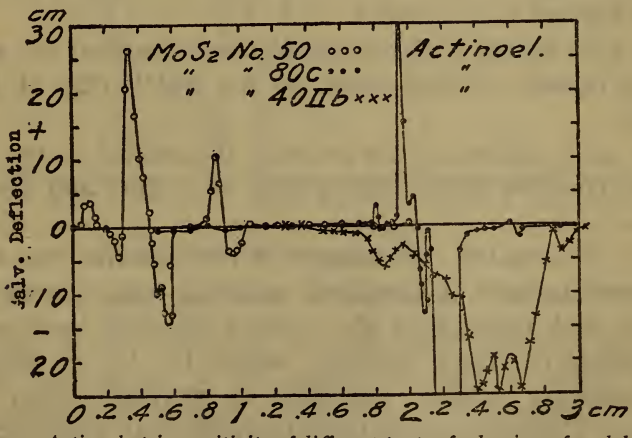

FIG. 2.—*Actinoelectric sensitivity of different parts of a lamina of molybdenite.*

Although these sharp maxima of + and − emf would be obtained by heating the two junctures of a thermocouple, the variety of data presented in this paper make it highly improbable that this is a thermal emf caused by, say, a filament of iron oxide imbedded in molybdenite.

Samples No. 80 No. 80A, No. 75 and No. 40A.—These are conspicuous in not exhibiting photoelectrical sensitivity under an impressed potential.

Sample No. 50.—The actinoelectrical sensitivity curve of different parts of molybdenite, sample No. 50, is given in Figure 2. The actinosensitivity is confined to about 1 cm length of this lamina. Figure 7 gives a magnified view of the actinoelectrical sensitivity, as well as the photoelectrical sensitivity curves of this sample of molybdenite as dependent upon the direction of the applied potential, which will be discussed on a subsequent page.

Sample No. 40IIb.—This sample is conspicuous in being composed of two parts, one of which gives a positive, the other a negative emf. (See Tables 1 and 2.) On the other hand, as shown in Figure 2, only one end is actinoelectrically sensitive, from which it would appear that there is no relation between these two phenomena.

Sample No. 75.—This was a thin narrow sample of material, size 12 by 2.5 by 0.25 mm. As shown in Figure 3 this sample exhibited practically no actinoelectrical sensitivity throughout its whole length. Furthermore it was insensitive photoelectrically.

Samples No. 40A and 40B.—Crystal No. 40 yielded lamina having unusual reactions throughout their whole length, as shown in Figures 3, 4, 5, and 6.

In No. 40A, Figure 3, the actinoelectrical reactions (+ and −) are about equally divided, while in No. 40IIb (fig. 2) the emf is negative.

In No. 40B, Figure 6, the reaction is confined in two widely separated complex spots, one giving a + emf and the other a − emf.

1. Iron Molybdate.—A sample of molybdenite was selected from several pounds of Canadian material which showed, over its surface and throughout the various cleavage laminas, thin, long filaments of yellow material, which Dr. W. F. Hillebrand of the chemistry division identified as molybdic ocher, called molybdite. This is a hydrous ferric molybdate, to which Schaller[33] has given the following formula: $Fe_2O_3 3MoO_3 . 7\frac{1}{2}H_2O$.

A thin yellow-colored needle (length 3.5 mm width 0.2 mm) of molybdite was isolated from the molybdenite lamina, and the ends were pressed in V-shaped electrodes of tinfoil. When

[33] Schaller, Amer. Jour. Sci., 23, p. 297; 1907.

exposed, in the usual manner, to the tungsten lamp, it showed no actinoelectrical sensitivity.

In the second test a lamina of molybdenite (6 mm long and 0.5 mm wide) attached to which was a molybdite crystal, 2.5 by 0.2 mm was exposed to radiation in the usual manner. This combination showed no actinoelectrical sensitivity. Furthermore, when touched with a hot wire, as described under Section IV, it showed no thermal emfs.

Evidently the actinoelectrical reaction in molybdenum is not to be attributed to the hydrous molybdate of iron.

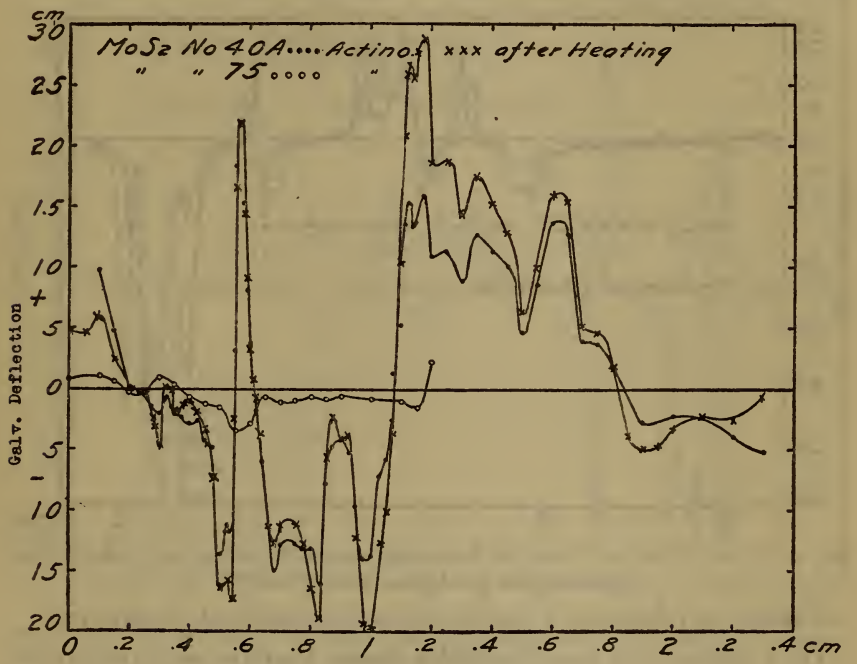

FIG. 3.—*Effect of heat treatment upon the actinoelectric sensitivity of different parts of a lamina of molybdenite.*

(b) EFFECT OF HEAT TREATMENT UPON ACTINOELECTRICAL SENSITIVITY.

In view of the possibility of molybdenite having microscopic, invisible, inclusions of molybdite, described under the preceding section, it seemed of interest to determine the effect of heat treatment upon actinoelectrical sensitivity, especially upon lamina split from molybdenite crystal, No. 40, which exhibits unusual thermoelectrical and actinoelectrical properties. The sample of molybdenite was therefore mounted and examined for actinoelectrical sensitivity in the usual manner. This sample was then dehydrated by baking in an oven for several hours.

Sample No. 40A.—The actinoelectrical sensitivity curves of different parts of sample No. 40A, before and after dehydration, are depicted in Figure 3. The maxima are practically identical in position and in intensity.

Taking into consideration the fact that this sample had to be dismounted for heat treatment, it would appear that any chemical changes brought about by heat treatment had no marked effect upon the actinoelectrical sensitivity of the material, except, perhaps, in the region 1.2 cm (see fig. 3), where the intensity of the actinoelectrical reaction seems to be greater after heating.

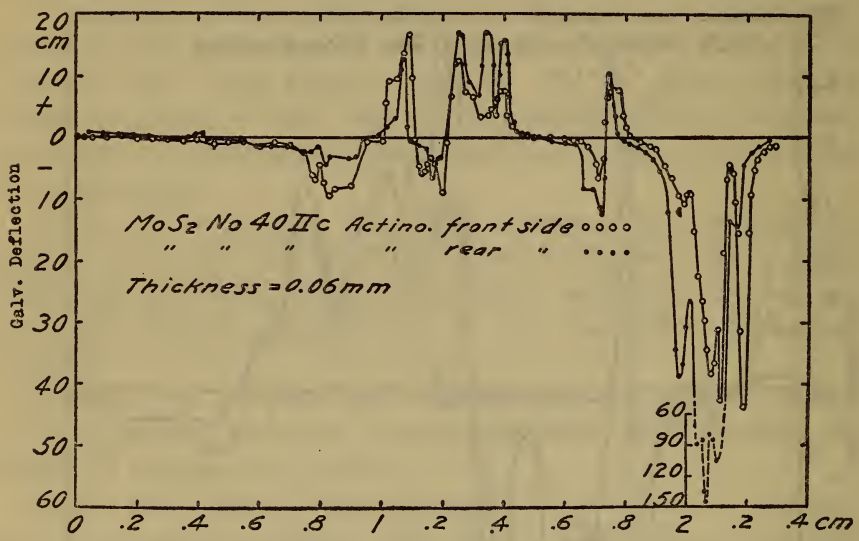

FIG. 4.—*Effect of thickness (depth of penetration) upon the actinoelectric sensitivity of different parts of a lamina of molybdenite.*

(c) EFFECT OF THICKNESS OF LAMINA UPON ACTINOELECTRICAL SENSITIVITY.

On a subsequent page it will be shown that the actinoelectrical reaction is caused by radiation of wave lengths less than 1 μ which are considerably absorbed by molybdenite. It was, therefore, of interest to determine the actinoelectrical reaction as viewed from the front and the rear sides of the sample.

In Figure 4 is shown the effect of thickness (depth of penetration) upon the actinoelectrical sensitivity of different parts of molybdenite, sample No. 40IIc, thickness 0.06 mm. In a few cases the loci of actinosensitivity seem to lie closer to one side (for example, at position 1.35 to 1.4 cm and at 1.98 to 2.1 cm) while others are more affected from the opposite side (for example, at position 1.1 and 2.2 cm). This is probably to be expected, even in a layer only 0.06 mm thick.

In Figure 5, samples 40IIc and 40IId illustrate the effect of thickness (contiguous, superposed layers) upon the actinoelectric sensitivity of different parts of a lamina of molybdenite. They were split from a lamina 0.2 mm in thickness. The actinoelectric sensitivity curves are entirely different, showing that, whatever the cause of this phenomenon, it is localized in a very small spot. This is further illustrated in sample 40IId at the (horizontal) positions 1.78 cm and 1.80 cm where the emfs are opposite in sign and the maxima are separated by only 0.2 mm.

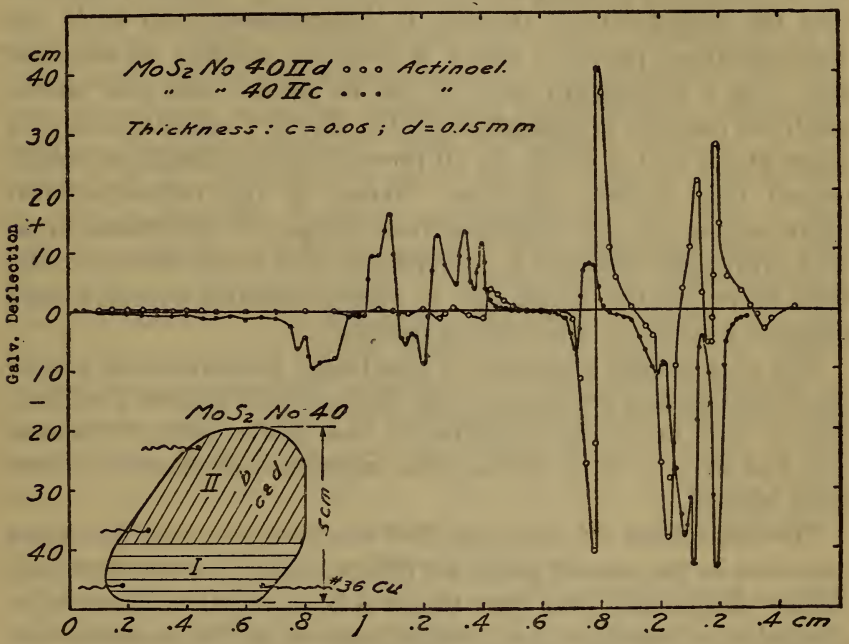

FIG. 5.—*Effect of thickness (superposed layers) upon the actinoelectric sensitivity of different parts of a lamina of molybdenite.*

Insert: Sketch of crystal from which laminas were taken.

From the foregoing data on various lengths and thicknesses of material it appears that the loci of actinoelectrical reaction are often confined to regions not more than 0.1 to 0.2 mm in diameter.

This was further verified by selecting a spot which showed a maximum sensitivity as observed with the vertical slit and exploring it with a slit, 0.2 mm wide, held horizontally. By raising and lowering the latter, thus exposing successive areas, 0.2 by 0.2 mm, it was found that the maximum sensitivity was equally sharp when the surface of the crystal was examined widthwise, as already described.

(d) ACTINOELECTRICAL AND PHOTOELECTRICAL REACTIONS IN DIFFERENT PARTS OF A LAMINA.

Under the present caption are described some of the most complex and perplexing phenomena the writer has yet found in this domain.

The term *photoelectric* is used simply to indicate that the test was made using an impressed emf in series with the crystal and the galvanometer. Under these conditions, using material having a high actinoelectrical sensitivity, but low photoelectrical sensitivity, it is found, on exposure of the sample to thermal radiation, that the photoelectrical reaction is instantaneous, just as in the actinoelectrical reaction, which is observed without an external emf. On a subsequent page it will be shown that this photoelectrical reaction is instantaneous for all wave lengths, including those at 0.8 to 1 μ which, in all previous investigations of solids, caused only a slow reaction. Hence, if the hereindescribed phenomenon is a true photoelectrical reaction, it is different from that previously observed in molybdenite and other solids, for the same wave lengths, where one to several minutes exposure were required to produce a maximum reaction.

The only similar examples of practically instantaneous photoelectrical reaction are the gas-ionic photoelectric cells of the alkali metals, and the photo-ionization in the halide salts of thallium lead and silver [34], in all of which the reaction is produced by short wave lengths.

Another reason for believing that the photoelectrical reactions described in the present paper are different from the reactions previously described is that there seems to be no relation between the photoeletrical reaction and the dark current in the crystal as observed on reversal of the applied potential (see fig. 7). For example, in one test of sample No. 50, the photoelectrical deflection for C. R. (dark current = 25 cm) was 9 cm as compared with only 2 cm for C. D. (dark current = 33.5 cm). In molybdenite, sample No. 1 previously examined, the photoelectrical reaction is the same for C. D. and C. R. when reduced to the same dark current.

It is of interest to note that in samples taken from the same crystal, for example, No. 40, Figure 5, some exhibit actionoelectrical, but no photoelectrical sensitivity. Other samples exhibit photoelectrical and actinoelectrical sensitivity in different parts of the same crystal. In a third class of crystals of molybdenite there appears to be a close coincidence of some of the loci of maximum actinoelectric and photoelectrical sensitivity. It is in this class of

[34] B. S. Sci. Papers (No. 456), 18, p. 489; 1922.

crystals that some extraordinary photoelectrical phenomena are observed, depending upon the direction of the impressed battery current through the crystal. As mentioned elsewhere, in this case the actinoelectrical reaction seems to function like a valve which augments or suppresses the photoelectrical reaction, depending upon the direction of the current through the crystal. In some cases this is so marked that only when the battery current passes through the crystal in the proper direction does the spot appear to exhibit photoelectrical sensitivity.

1. RADIOMETRIC TEST.—It seemed of interest to compare the actinoelectric effect (galvanometer deflection) with that of a (radiometer) thermocouple exposed to the same radiation stimulus. For this purpose a copper-constantan thermocouple, previously used in planetary radiation [35] work, having a receiver 1.5 by 2.2 mm (in air) was connected in series with molybdenite, sample No. 50, and an ironclad Thomson galvanometer. The size of the radiation stimulus (using the crossed slits previously described) was 0.2 by 0.2 mm. Exposing the thermocouple to this radiation stimulus produced a galvanometer deflection of about 3.5 mm. Exposing the sensitive spot in sample No. 50, marked V in Figure 7, caused a galvanometer deflection of 42 mm, or 12 times that of the thermocouple. Owing to high transmission and reflection, the molybdenite sample did not utilize more than, perhaps, 60 per cent of the incident radiation. From the test of thermoelectric power (Table 2, −180 mv) there appears to be no relation between the thermoelectric and the actinoelectric data.

From this it is evident that this sample would form a good radiometer, using only a selected part of the spectrum. By properly combining it in a battery circuit this device could be used as a photoelectric radiometer.

2. ACTINOREACTIVE MOLYBDENITE WHICH IS NOT SENSITIVE PHOTOELECTRICALLY.—Molybdenite samples Nos. 40A, 40IIb, 75, 80, 80A, and 80C were tested for photoelectrical sensitivity at 22° C., but no reaction was observed. An examination should be made at low temperatures, under which conditions it was previously found that some samples of molybdenite exhibit photoelectrical sensitivity.

It may be added that samples Nos. 40IIb and 80C, Figure 2, were reexamined thoroughly, in the regions of maximum actinoelectrical sensitivity, but no photoelectrical reaction could be detected.

[35] B. S. Sci. Papers (No. 460), 18, p. 540; 1922.

3. Samples Exhibiting Photoelectrical and Actinoelectrical Sensitivity.—A number of samples of molybdenite were found which exhibit photoelectrical and actinoelectrical sensitivity in the same or closely adjoining spots.

Sample No. 40B.—The examination of a sample throughout its whole length is time consuming, and only a few have been thus examined. In Figure 6, the circles (○○○) show the actinoelectrical reaction of molybdenite, sample No. 40B. This sample is interesting in having a wide region of positive actinoelectrical sensitivity near the end of the sample and a similar region of negative actinoelectrical sensitivity at the other end of the crystal.

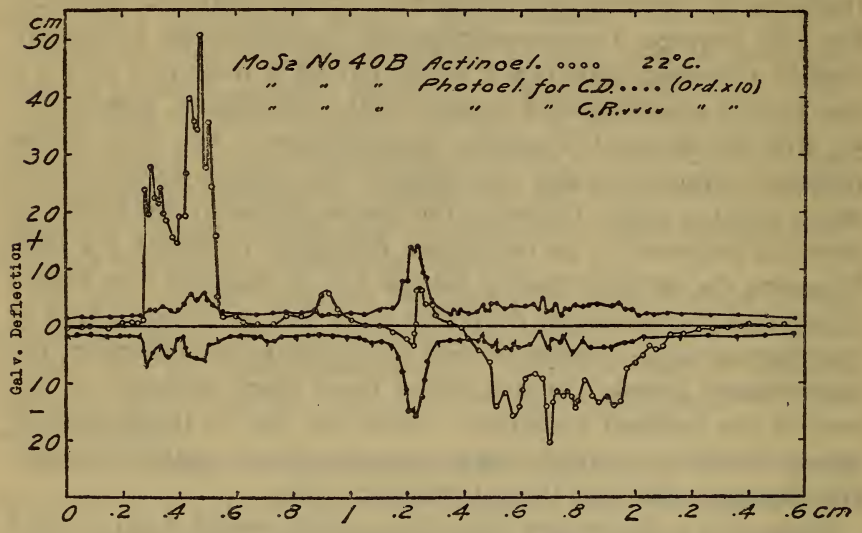

Fig. 6.—*Actinoelectric and photoelectric sensitivity of different parts of molybdenite. Sample No. 40B*

The galvanometer deflections, in cm, were observed with an iron-clad Thomson galvanometer.

The photoelectrical reactions for the current direct (C. D . . .) and reversed (C. R. , , ,) Figure 6, were observed with a d'Arsonval galvanometer, the observations being magnified 10 times.

This sample seems to be practically insensitive photoelectrically (at 22° C.) except in the region p = 1.2 cm from the left-hand electrode, which is conspicuous for an abrupt change from negative to positive actinosensitivity. The intensity of the photoelectrical reaction does not depend upon the direction of the impressed battery potential, which caused a dark current (galvanometer deflection) of 24 cm for C. D. and 23 cm for C. R., which is sufficiently large to detect a change in resistance of a sample of average photoelectric sensitivity.

Sample No. 50.—This sample is one of the most interesting yet found, ranking with sample No. 1 (previously studied) in unusual electrical properties.

The actinoelectrical reactions of the light-reactive end (see fig. 2) of the lamina are depicted on a large scale in Figure 7 (○○○). In this illustration the strong maxima of positive and negative emf are marked I, II, III, etc., for convenient reference in the spectrophotoelectrical tests described on a subsequent page.

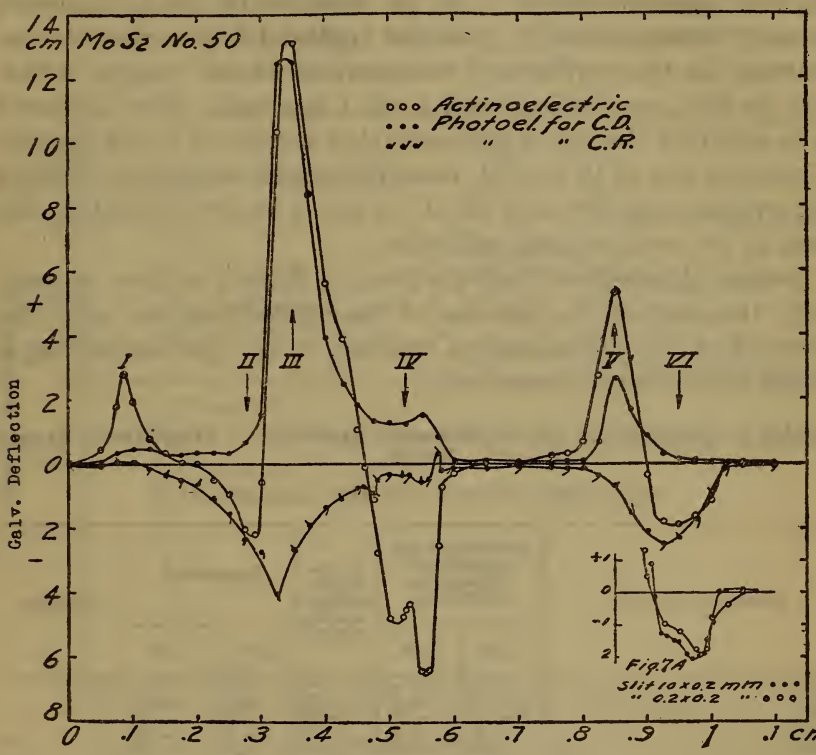

FIG. 7.—*Actinoelectric and photoelectric sensitivity of different parts of molybdenite. Sample No. 50*

In this sample the light-reactive spots are notable for their width and intensity of response. A further and extensive examination was therefore made of these light-sensitive areas. For this purpose the maximum of sensitivity of each spot was located by moving the radiation stimulus (0.2 by 0.2 mm area) vertically (widthwise) across the lamina, then making the exploration lengthwise. As shown in Figure 7A (see fig. 7), which depicts the light-sensitive area VI, there is practically no difference in the position and general outline of the (complex) maximum, using the slit 10 by 0.2 mm (plotted . . .) and the one of 0.2 by 0.2 mm

(plotted ○○○; ordinates ×150), when a minute examination is made of these spots.

The photoelectrical reaction curves for the current direct (C. D.) and reversed (C. R.) are illustrated with dots (. . .) and commas (, , ,), respectively, in Figure 7. In these tests one dry battery (1.4 volts) was used, the dark current being +10.5 cm for C. D. and −25.5 cm for C. R.

The first thing to be noticed is that the maxima of the photoelectrical reaction depend upon the direction of the dark current passing through (that is, potential applied to) the crystal. For example, in the preliminary examination of this sample, which was the first one studied using a slit 1 mm wide, there appeared to be an entire absence of photoelectrical sensitivity in the maxima of negative emf at IV and VI, when the current was passed through the crystal in the direction (C. D.) to give a positive deflection, the same as the actinoelectric deflection.

Some of the observed data are given in Table 3 to show, numerically, the effect of the direction of the applied potential upon the intensity of the photoelectrical reaction, in the spots exhibiting a strong actinoelectrical reaction.

TABLE 3.—Photoelectric and Actinoelectric Sensitivity of Molybdenite Sample No. 50.

[Dark current=+15.3 cm for C. D. and −21.1 cm for C. R.]

Position in centimeters.	Photoelectric and actinoelectric deflection in centimeters.		Actinoelectric deflection in centimeters.	Photoelectric.		Remarks.
	C. D.	C. R.		C. D.	C. R.	
0.750	+0.17	−0.07	+0.06	+0.11	−0.13	
0.775	+.22	−.08	+.10	+.12	−.18	
0.800	+.28	−.02	+.17	+.11	−.19	
0.825	+1.41	+.22	+.69	+.72	−.47	
0.850	+3.94	+.68	+1.33	+2.61	−.65	Maximum positive emf.
0.875	+2.48	−.67	+.83	+1.65	−1.50	
0.900	+.79	−2.18	−.09	+.88	−2.09	
0.925	−.20	−2.94	−.45	+.25	−2.49	Maximum negative emf.
0.950	−.28	−2.74	−.47	+.19	−2.27	
0.975	−.28	−2.21	−.42	+.14	−1.79	
1.000	−.20	−1.15	−.27	+.07	−.88	

These data show that instead of obtaining the same photoelectrical reaction (the same galvanometer deflection) on reversal of the battery current, as found in sample No. 1, in sample No. 50, which is conspicuous for its high actinoelectrical sensitivity, there is an outstanding difference of 2 to 10 times between the maximum and the minimum photoelectrical effects.

The photoelectrical reaction in the region of IV in Figure 7, is the reverse of that observed in the other bands of negative actinoelectrical sensitivity.

Sample 40IId.—After the thorough examination of sample No. 50 it seemed sufficient to examine only isolated points in other samples. The sharp positive and negative maxima of actinoelectrical sensitivity at p = 1.76 and p = 1.79, respectively, in Figure 5, are sufficiently isolated to give good results in the photoelectrical tests. The sample, in the meantime, having been remounted on its holder (which had a fixed scale attached thereto), the maxima of these two bands are given at p = 1.65 and p = 1.69

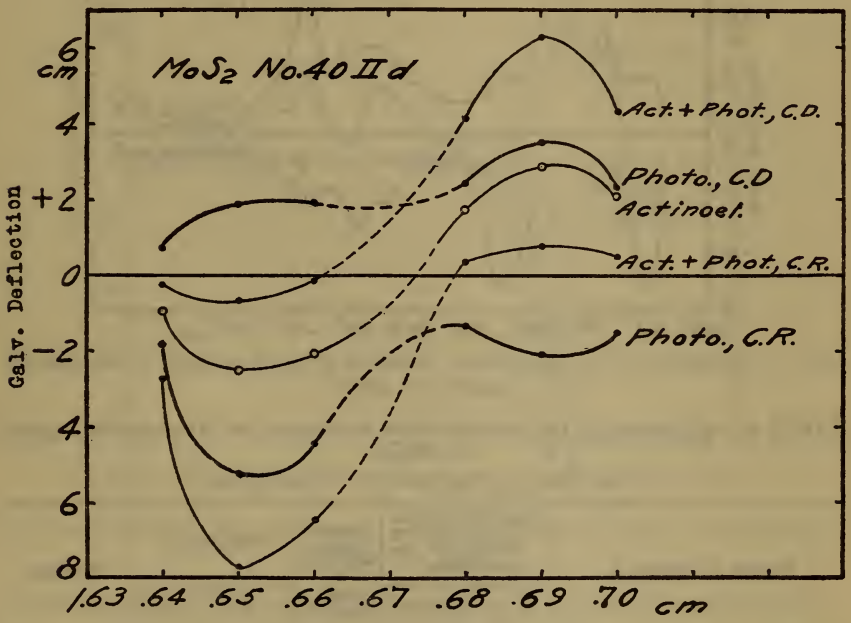

FIG. 8.—*Actinoelectric and photoelectric sensitivity of different parts of molybdenite Sample No. 40IId*

in Figures 8 and 9. Similarly the observations at p = 2.0 to p = 2.3 in Figure 5 are given at p = 1.9 to p = 2.2 in Figure 9.

As shown in Figure 8 when the external battery is applied so that the dark current is in the same direction as the actinoelectric current then the photoelectrical reaction current is 2.6 to 3 times that observed when the dark current flows in the opposite direction. In other words, the ionization is increased or decreased depending whether the battery (1.4 volts) is applied as an accelerating or retarding potential.

In Figure 8 all the observed as well as calculated reactions are plotted as obtained from Table 4. For simplification, in Figure 9

only the observed actinoelectrical reaction and the (calculated) pure photoelectrical reactions are depicted. The photosensitive spots being so close together at p = 1.9 to p = 2.2 there were great difficulties in resetting on exactly the same spots. But even in this part of the crystal the photoelectrical reaction is amplified or diminished depending upon the direction of the impressed potential. For example, in the spot of negative actinoelectrical sensitivity at p = 1.93 the intensity of the photoelectrical reaction is varied by the factor 2.6 on reversal of the battery current.

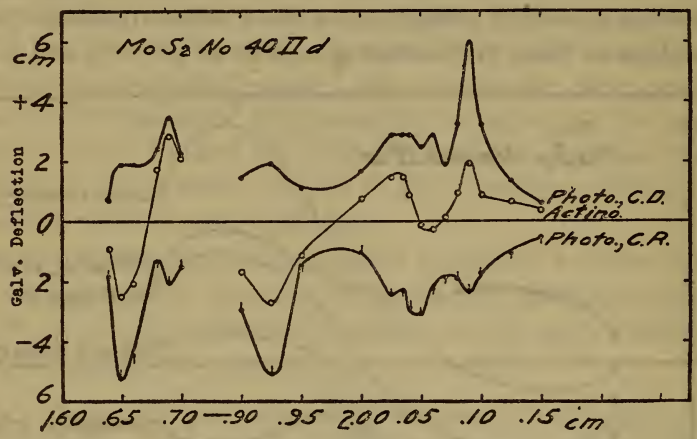

FIG. 9.—*Actinoelectric and photoelectric sensitivity of different parts of molybdenite. Sample No. 40IId*

TABLE 4.—Photoelectric and Actinoelectric Sensitivity of Molybdenite Sample No. 40IId.

[Dark current = +17 cm for C. D.; −20 cm for C. R.]

Position in centimeters.	Photoelectric plus Actinoelectric deflection in centimeters.		Actinoelectric deflection in centimeters.	Photoelectric.		Remarks.
	C. D.	C. R.		C. D.	C. R.	
1.640	−0.23	−2.77	−0.96	+0.73	−1.81	
1.650	−.66	−7.73	−2.51	+1.85	−5.22	Maximum negative emf.
1.660	−.18	−6.48	−2.06	+1.88	−4.42	
1.680	+4.14	+.36	+1.74	+2.40	−1.38	
1.690	+6.28	+.76	+2.83	+3.45	−2.07	Maximum positive emf.
1.700	+4.30	+.48	+2.06	+2.24	−1.58	
1.900	−.29	−4.70	−1.70	+1.41	−3.00	
1.925	−.76	−7.80	−2.74	+1.98	−5.06	Maximum negative emf.
1.950	−.09	−2.62	−1.16	+1.07	−1.46	
2.000	+2.40	−.24	+.77	+1.63	−1.01	
2.025	+4.30	−.94	+1.47	+2.83	−2.41	
2.035	+4.31	−.91	+1.42	+2.89	−2.33	Maximum positive emf.
2.040	+3.69	−2.12	+.83	+2.86	−2.95	
2.050	+2.33	−3.20	−.12	+2.45	−3.08	Maximum negative emf.
2.060	+1.59	−2.52	−.26	+1.85	−2.26	
2.070	+2.00	−1.81	+.10	+1.90	−1.91	
2.080	+4.15	−1.04	+.94	+3.21	−1.98	
2.090	+7.88	−.42	+1.93	+5.95	−2.35	Maximum positive emf.
2.100	+4.03	−.91	+.83	+3.20	−1.74	
2.125	+1.97	−.42	+.63	+1.34	−1.05	
2.150	+.99	−.13	+.39	+.60	−.52	

Sample No. 40IIc. In Figure 4 is depicted the actinoelectrical reaction for the whole length of the crystal No. 40IIc as viewed from the front side (○○○). In Figure 10 are depicted the actinoelectrical and the pure photoelectrical reactions (as deduced on a preceding page) for selected positions, p = 0.8 to 1.2 and p = 1.6 to 2.2 cm along the length of the crystal.

In that part of the crystal marked p = 1.8 to 2.2 the photoelectrical reaction on reversal is amplified or reduced, the factor being about 2 to 2.2, the dark currents giving −15.8 cm and +31.5 cm (C. D.) deflection, respectively.

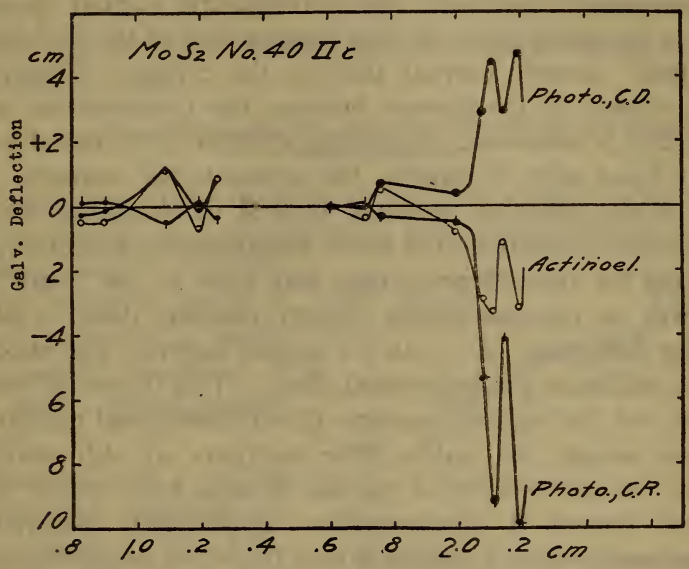

FIG. 10.—*Actinoelectric and photoelectric sensitivity of different parts of molybdenite. Sample No. 40IIc*

In some parts of this crystal showing actinoelectrical sensitivity, for example, at p = 1.2, the photoelectrical reaction is inappreciable.

In some parts of this sample, for example, at p = 0.8 to 0.9 cm and at p = 1.2 the electrical reaction seems to be photonegative instead of being electrically photopositive as usually observed. In other words, the photoelectrical reaction is just the reverse of what would be expected from the direction of the dark current through the crystal. This is of rare occurrence, especially at room temperature.[36]

As already mentioned, in previous investigations of molybdenite, in which the actinoelectrical reaction is inappreciable, the photoelectrical reaction was found to be independent of the direction of the battery current through the crystal.

[36] B. S. Sci. Papers 398 and 462.

In the foregoing pages molybdenite samples are described in which the actinoelectrical reaction seems to function like a valve, which amplifies or reduces the photoelectrical reaction, depending upon the direction of the impressed battery current through the crystal. For example, after deducting the actinoelectric current (galvanometer deflection, observed without the impressed emf) from the combined photoelectric and actinoelectric current (galvanometer deflection observed when there is an external emf) there remains what is supposed to be the true photoelectric current, which is a measure of the photoelectrical reaction. Now, from previous experiences, this photoelectric current should be found to be proportional to (but independent of the direction of) the "dark" battery current through the crystal. However, as already stated, in the present instance the photoelectric current is amplified or weakened, depending whether the external battery current flows with or against the actinoelectric current. As a result of this selective response, instead of obtaining the same photoelectrical reaction (the same galvanometer deflection, after correcting for any difference that may exist in the "dark" conductivity) on reversal of the battery current, there is an outstanding difference, of 1.5 to 2.5 times, between the maximum and the minimum photoelectrical effect. This is true of both the positive and the negative maxima of actinoelectrical reaction.

In one sample, No. 40IIc, these reactions are still more complicated, the photoelectrical reaction in some spots being "photonegative" instead of "photopositive" as ordinarily observed.

These results seem to indicate that the whole phenomenon may not be so dependent upon the unipolar conduction of the whole crystal as would appear from these tests. The next thing to be done is to isolate the spots exhibiting high actinoelectrical sensitivity and examine them separately. This will be a tedious, time-consuming undertaking. The material is of rare occurrence and the risk of injury or loss is too great to attempt to attain the goal in one step. Hence, as much information as seemed useful was obtained on the large lamina before attempting to excise the parts of the lamina containing the sensitive spots, and subject them to investigation.

In conclusion it is to be noted that the spots which exhibit an actinoelectrical reaction, when exposed to light, become a source of impressed emf to the loci of photoelectrical sensitivity. However, as measured in terms of the (dark) current through the galvanometer this effect appears to be small.

3. SPECTRAL RADIATION MEASUREMENTS.

The actinoelectrical and photoelectrical sensitivity of various samples of molybdenite in the visible and in the infra-reds pectrum was determined by means of a mirror spectrometer, quartz prism, and a 500-watt gas-filled tungsten lamp, as described in previous papers.[37] In the visible spectrum the data were supplemented by measurements with a lens spectrometer and a glass prism.[38]

The radiation intensities (E = 1, E = 14) were applied in the form of an equal energy spectrum by varying the temperature of the lamp, as in previous work. Unless otherwise noted (for example, at low temperatures) the samples were exposed at the exit slit of the spectrometer.

(a) SPECTROACTINOELECTRIC SENSITIVITY OF VARIOUS SAMPLES OF MOLYBDENITE.

In addition to the determination of the manner of distribution of the maxima of actinoelectrical and photoelectrical sensitivity in the crystal, as described in the foregoing pages, it was of interest to study the spectral reactions of of these photosensitive spots.

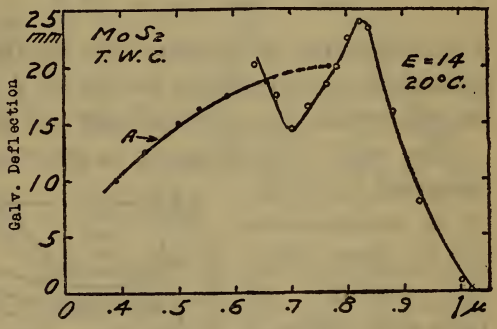

FIG. 11.—*Spectroactinoelectric sensitivity of a sample of molybdenite.* (*Case*)

Sample T. W. C.—This sample of molybdenite was loaned by the Case Research Laboratory. It was mounted in an evacuated glass container. This crystal, which was about 8 mm long between the electrodes, appeared to have but one large photosensitive spot.

The actinoelectrical sensitivity as observed with a lens spectrometer is given in curve *A*, Figure 11. A more thorough examination with a mirror spectrometer shows a minimum in the region of 0.7 μ. Other samples which do not show this minimum, or which have the indentations at other wave lengths, are given in the following illustrations. Suffice it to add that, so far as is now known, there appears to be no relation between these maxima and minima of photosensitivity, and the maxima and minima of trans-

[37] B. S. Sci. Papers Nos. 338, 398, 412, and 446.
[38] B. S. Bull., 14, p. 166; 1917 (No. 303).

mission and reflection recorded in previous papers.[39] Neither do they appear to be connected with either the negative or the positive actinoelectric reaction.

Sample No. 50.—The spectral responses of the spot marked *III* in Figure 7, as observed with the mirror spectrometer are given in Figure 12 (see also fig. 13). The galvanometer deflections for the two intensities, are not comparable, in view of the fact that the measurements were not made for that purpose. The indentations at 0.7 and 0.85 μ are noteworthy.

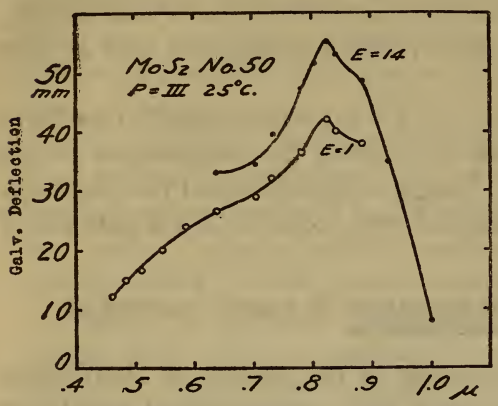

FIG. 12.—*Spectroactinoelectric sensitivity of molybdenite. Sample No. 50*

The spectral actinoelectric reactions of the positive and negative maxima, marked *I*, to *V* in Figure 7 are depicted in Figure 13. In this illustration the observed galvanometer deflections for curves *I* and *IV* are plotted to scale in mm, while for curves *II* and *III* the scale is divided by two.

The spot exhibiting a negative actinoelectrical sensitivity (marked *II* in fig. 7) is conspicuous for its three spectral maxima, at 0.60, 0.66, and 0.92 μ, respectively, with a deep minimum at 0.8 μ where there is usually found a maximum spectral photoelectric response. The measurements were made with radiation intensities E=7 and E=14, from which it would appear that this minimum is not owing to experimental errors, or different intensities.

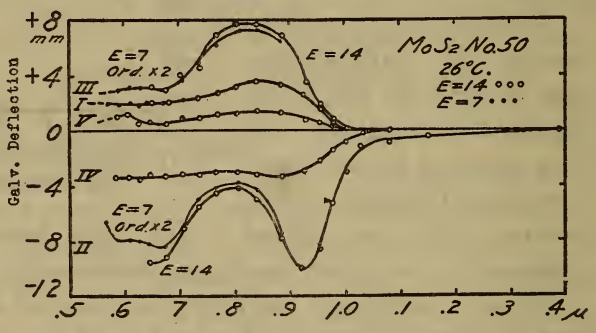

FIG. 13.—*Spectroactinoelectric sensitivity of different parts of molybdenite. Sample No. 50*

Sample No. 1.—Data on the spectral actinoelectrical reaction of molybdenite sample No. 1 are given in Figure 16, in which

[39] Coblentz and Kahler, B. S. Sci. Papers, 15, p. 121, 1919 (No. 338); Tyndall, Phys. Rev. (2), 21, p. 163; 1923.

curve *A* represents the observations obtained with a lens spectrometer. The spot examined was probably P–3 which showed [40] a complex photoelectrical reaction.

Sample No. 8.—In Figure 18, curve A gives the spectral actinoelectric reaction of sample No. 8 (see B. S. Sci. Paper No. 338) as observed with a lens spectrometer. Curve B, which was obtained with a mirror spectrometer, shows that the actinoelectrical reaction consists of a single spectral band, with a maximum at 0.8 μ. This sample seemed to have only one large sensitive spot.

(c) EFFECT OF THICKNESS OF LAMINA UPON SPECTROACTINOELECTRIC SENSITIVITY.

From the observations on the effect of depth of penetration of the radiation stimulus upon actinoelectrical sensitivity as observed by viewing the front and rear side of a thin sample of molybdenite, Figure 4, or as observed in two laterally contiguous lamina, Figure 5, there may be some question whether the following observations give all the information desired.

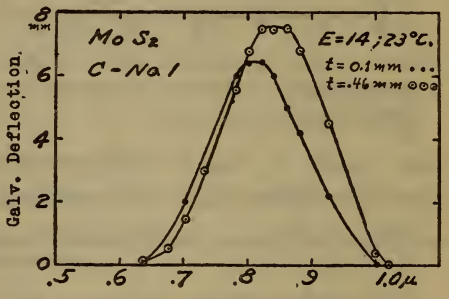

FIG. 14.—*Effect of thickness upon the spectroactinoelectric sensitivity of molybdenite. Sample C–No. 1*

Sample C. No. 1.—This sample was split from a crystal of molybdenite supplied by the Case Research Laboratory. The lamina as first examined was 0.46 mm in thickness, and it appeared to have only one large area exhibiting actinoelectrical sensitivity. In splitting it into thinner laminas, only one remained which was in good condition.

The spectral actinoelectric sensitivity curves of these two samples (thicknesses 0.1 and 0.46 mm, respectively) are given in Figure 14. There is but one maximum, at 0.81 μ which shifts to 0.84 μ for the thicker sample. This shift is to be expected if the reaction is a function of the absorption (thickness) of the material, which decreases rapidly in absorption with increase in wave length in this region of the spectrum.

This sample was insensitive photoelectrically as tested with a 16-cp. tungsten filament incandescent lamp, which was held close (2 cm) to the sample.

[40] B. S. Sci. Papers, 16, p. 608; 1920 (see fig. 7).

Sample No. 33.—This sample was split from the Australian material which is sensitive photoelectrically (see Table 1). In its original thickness 0.49 mm (area 6 by 5 mm) this sample exhibited marked photoelectrical sensitivity, but seemed to be insensitive actinoelectrically. It was, therefore, reduced to 0.25 mm in thickness, and finally to 0.055 mm thickness. Under these conditions the material exhibited actinoelectrical sensitivity, the galvanometer deflections for the thicker sample being twice as large (maximum = 7 mm) as for the thinner sample.

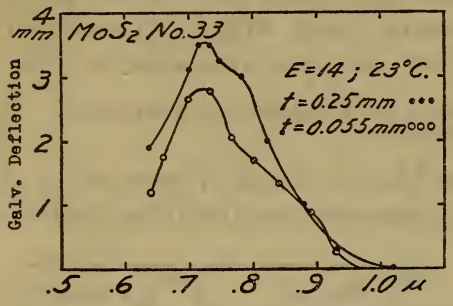

FIG. 15.—*Effect of thickness upon the spectroactinoelectric sensitivity of molybdenite. Sample No. 33*

The spectroactinoelectrical reaction curves are given in Figure 15. The curves are complex, indented, and it is difficult to determine how much of this is owing to the effect of depth of penetration (absorption) upon the spectral reaction.

(c) EFFECT OF INTENSITY OF RADIATION STIMULUS UPON SPECTROACTINOELECTRIC SENSITIVITY.

In previous tests of spectrophotoelectrical sensitivity it was found that with increase in intensity the reaction increases more rapidly on the long wave length side of the maximum than on the side toward the short wave lengths. Furthermore, there is no direct proportionality between the intensity of the radiation stimulus and the photoelectrical reaction.

From the results of the present tests it appears that the spectral actinoelectrical response, at least for low intensities, is more closely proportional to the intensity of the radiation stimulus, of different wave lengths, than was found for the photoelectrical reaction.

Sample No. 50.—The foregoing conclusions are based upon observations such as were obtained on sample No. 50, illustrated in Figures 12 and 13.

For example, the actinoelectric responses for E = 7 when multiplied by 2, and plotted as dots (. . .) superpose very closely and symmetrically upon the data obtained for E = 14, plotted as circles (○ ○ ○) in Figure 13. The one exception is that part of the curve between 0.55 and 0.65 μ observed in the spot, *II*, having an unusual actinoelectric reaction.

Sample No. 1.—In Figure 16 are depicted the actinoelectrical reactions of molybdenite sample No. 1 (probably close to the spot P–3[41]) for intensities E = 7 and E = 14. For the latter intensity the galvanometer deflections are reduced by one-half; but the two curves do not superpose as they should if there were a direct proportionality between the intensity of the radiation stimulus and the actinoelectric reaction.

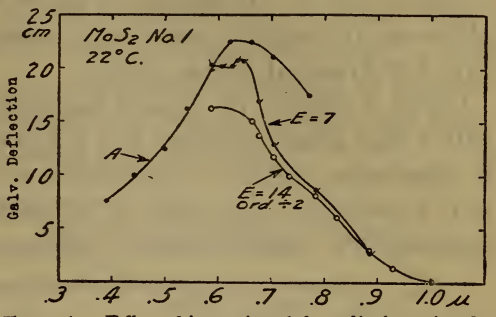

FIG. 16.—*Effect of intensity of the radiation stimulus upon the spectroactinoelectric sensitivity of molybdenite. Sample No. 1 at 22° C.*

In Figure 17 is depicted the actinoelectrical reaction of the photopositive region, P–4, at low temperatures, – 104° C. The sample being in an evacuated glass vessel, in liquid air as previously described (B. S. Sci. Paper No. 338), the intensities were only about one-fourth that previously observed.

The ratio of the radiation intensities = 7.4. The ratio of the observed maximum actinoelectric reaction = 6.2. Further data on the actinoelectrical reaction of the photopositive region, P–4, at 25° C., for E = 1.75 and E = 3.5 (sample in glass container as above) are given in the lower part of Figure 22. Here also there is no exact proportionality of the reaction at the maximum, although there is an exact coincidence on the long wave-length side of the maximum.

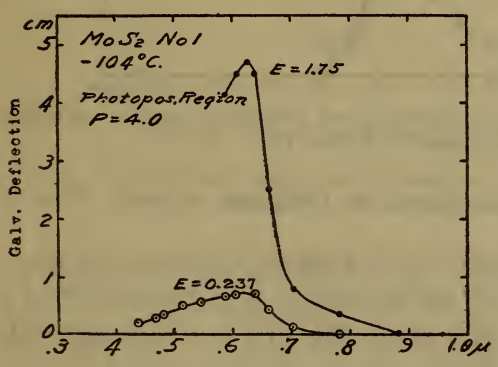

FIG. 17.—*Effect of intensity of the radiation stimulus upon the spectroactinoelectric sensitivity of molybdenite. Sample No. 1 at low temperature*

From the data at hand it appears that, if there is any dissymmetry in the spectral increase of the actinoelectric response, with increase in intensity of the radiation stimulus, it occurs on the short wave-length side of the maximum, instead of the long wave-length side of the maximum as observed in the spectral photoelectric reaction.

[41] See Figure 7, B. S. Sci. Papers No. 398, 16, p. 608; 1920.

(d) COMPARISON OF SPECTRAL ACTINOELECTRIC AND PHOTOELECTRIC SENSITIVITY.

Under the present caption it will be shown that the maxima of actinoelectric and photoelectric reaction occur in different parts of the spectrum.

Sample No. 8.—In Figure 18, curve C gives part of the spectral photoelectric reaction previously observed (B. S. Sci. Paper No. with a d'Arsonval galvanometer.

Curve A, Figure 18, depicts the actinoelectric reaction obtained with a lens spectronometer and a Thomson galvanometer. Curve B represents similar observations with a mirror spectrometer. It is to be noted that there is no similarity between the spectral actinoelectric reaction which terminates at 1 μ and the photo-

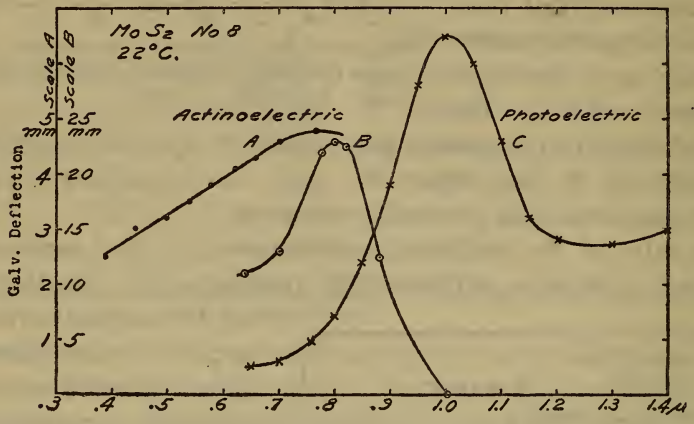

FIG. 18.—*Comparison of the spectral actinoelectric and photoelectric sensitivity of molybdenite. Sample No. 8 at 22° C.*

electric reaction which is produced by radiation stimuli of wave lengths extending to 2 μ.

Sample No. 1.—In Figure 19 is depicted the spectrophotoelectric reaction at $-104°$ C., for the region of the crystal P = 4.5 (see B. S. Sci. Paper No. 338) extending to 1.1 μ, although this sample is sensitive to 2 μ.

If the impressed battery current had passed through the crystal in the opposite direction, the deflection resulting from the photoelectric reaction would have been negative, and, hence, in the same direction as the observed actinoelectric reaction.

In this same illustration the lower curve represents the actinoelectric reaction at $-104°$ C. as observed with a sensitive Thomson galvanometer. Using a d'Arsonval galvanometer the deflection at the maximum (at 0.63 μ) was only 0.7 mm, which is negligible in its effect upon the photoelectrical measurements.

In Figure 21 is depicted the spectral photoelectric and actinoelectric reaction in the spot which exhibits photonegative sensitivity (B.S. Sci. Paper No. 398). In this case the spectral actinoelectric reaction passes from negative through zero to positive values, somewhat similar to the photoelectrical reaction, which, however, is sensitive to radiation of wave lengths beyond 2 μ. As shown in this illustration the actinoelectric reaction as observed with a d'Arsonval galvanometer was imperceptible and, hence, did not affect the photoelectrical measurements.

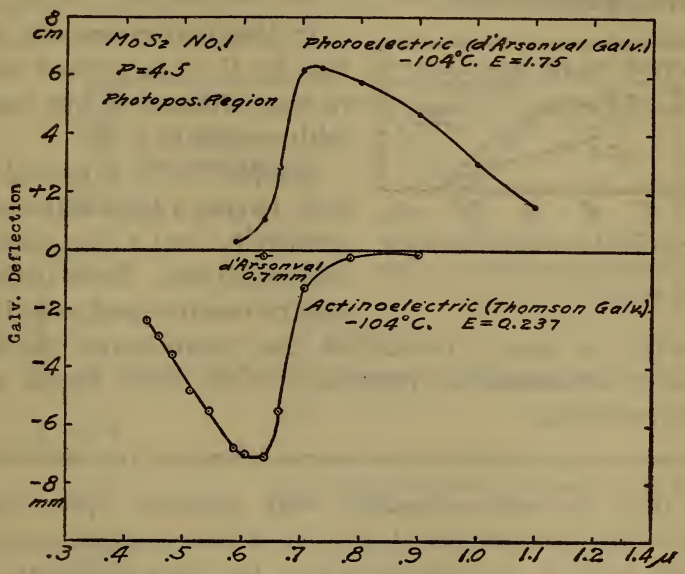

FIG. 19.—*Comparison of the spectral actinoelectric and photoelectric sensitivity of molybdenite. Sample No. 1 at low temperatures (photopositive spot)*

In this sample the spectral actinoelectric reaction, on exposure to radiation and the recovery after exposure, is practically instantaneous in the sense that it is completed in less time than is required (two seconds) for the galvanometer to execute a single swing. On the other hand, the time required to obtain the maximum spectral photoelectric reaction is a function of the wave length, requiring from one to several minutes, and twice that time for recovery after exposure, as described in B. S. Sci. Paper No. 338.

Sample No. 50.—In Figure 20 is shown the spectral photoelectric reaction and the actinoelectric reaction of the photosensitive spot P–III (see fig. 7) at 25° C. The dark current was 31.2 cm for C. D. and 14.4 cm for C. R. Nevertheless the

photoelectric reaction was twice as great for C. R. as for C. D. If the dark current were a measure of the photoelectrical sensitivity, as observed in previous investigations, then the galvanometer deflection for C. R. would have been twice the observed value. Furthermore the photoelectrical reaction was observed to be instantaneous (and terminated at 1 μ) which is contrary to previous experience.

The actinoelectrical reaction terminates at 1 μ, as previously observed in Figure 13. All these observations were made with a d'Arsonval galvanometer.

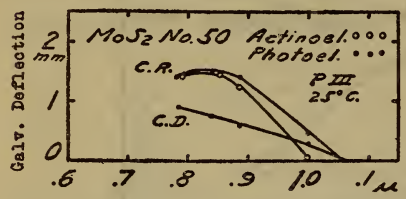

FIG. 20.—*Spectral photoelectric and actinoelectric sensitivity of molybdenite. Sample No. 50 (see fig. 7)*

In this illustration the deflection for C. D. is plotted positive in sign, although it was negative with respect to C. R.

Sample No. 50 is typical of the type having a high actinoelectric sensitivity and a low photoelectric sensitivity. Both the actinoelectric reaction and, what is more noteworthy, as already mentioned, the photoelectric reaction is practically instantaneous, regardless of the wave length of the radiation stimulus.

(e) EFFECT OF TEMPERATURE UPON SPECTROACTINOELECTRIC SENSITIVITY.

The data herewith presented were obtained upon material having a high photoelectrical, but low actinoelectrical sensitivity. Although there is no indication that the photoelectrically nonsensitive material will give materially different results, actinoelectrically, the subject should be given further investigation using material of low photoelectrical sensitivity.

Sample No. 1.—From the data given in Figures 16, 17, 19, and 22 it appears that, in that part of the lamina which exhibits the positive photoelectrical reaction, lowering the temperature from 25° C. to − 104° C. has no marked effect upon the general outline of the spectral actinoelectric reaction curve. For example, in the lower part of Figure 22 are plotted the actinoelectric observations on the photopositive region, P = 4.0, for the intensity E = 1.75, the temperatures being, respectively, 25° C. (plotted as commas ' ' ') and − 104° C. (x x x).

The maximum of the spectral reaction at 0.63 μ shifts but little with decrease in the temperature. The spectral limit of sensitivity at 0.78 to 0.85 μ is not very greatly affected by

temperature change, as previously observed in the photoelectrical reaction. The intrinsic sensitivity is greatly increased (perhaps five times at $-104°$ C.) with decrease in temperature.

On the other hand, in that part of the sample, P = 1.75, which exhibits the negative photoelectrical reaction, the intrinsic actinoelectric sensitivity seems to be greatly decreased at low temperatures. Moreover, the spectral actinoelectric reaction undergoes marked changes with variation in temperature.

In the upper part of Figure 21 a graphic comparison is made of the spectral photoelectric and actinoelectric reactions in the spot P = 1.75 at about $-104°$ C.

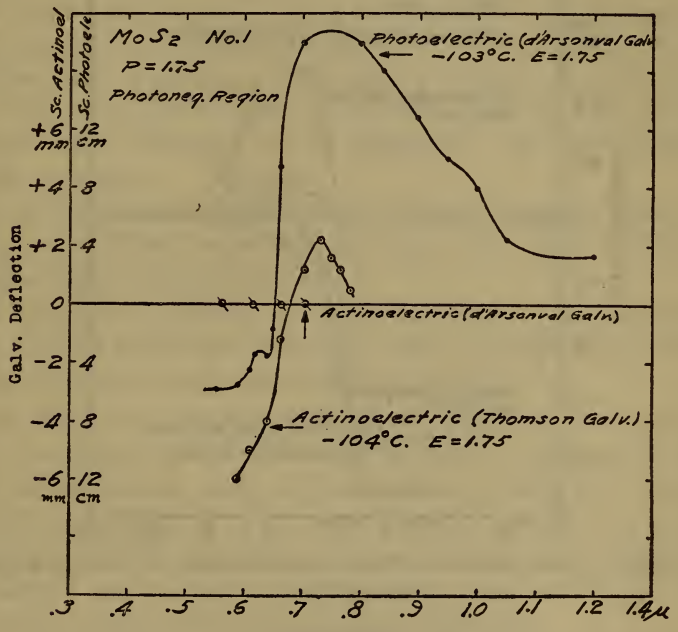

FIG. 21.—*Comparison of the spectral actinoelectric and photoelectric sensitivity of molybdenite. Sample No. 1 (photonegative spot)*

Using a d'Arsonval galvanometer, the deflections for the spectral actinoelectric reaction, as indicated in Figure 21, were too small to be observed. From this it appears that, as previously found, the actinoelectrical reaction had no effect upon the previously published measurements of spectrophotoelectrical sensitivity.

In Figure 22 is shown the spectral actinoelectric reaction of the spot P = 1.75 at 25° C. and $-98°$ C., respectively, when exposed to the radiation stimulus of intensity E = 3.5. At the lower temperature the intrinsic actinoelectric sensitivity seemed to be greatly

decreased, so that, for illustration in Figure 22, the ordinates have been magnified 10 times. This decrease, however, may be owing to the fact that the actinoelectrical emf was measured in terms of the current through the galvanometer, and no correction was made for the increase in resistance of the sample of molybdenite at low temperature.

It is to be noted that at the lower temperatures the negative galvanometer deflections remain relatively the same as at 25° C. On the other hand, the positive reaction at 0.78 to 1 μ has disappeared relatively to that observed at 25° C.

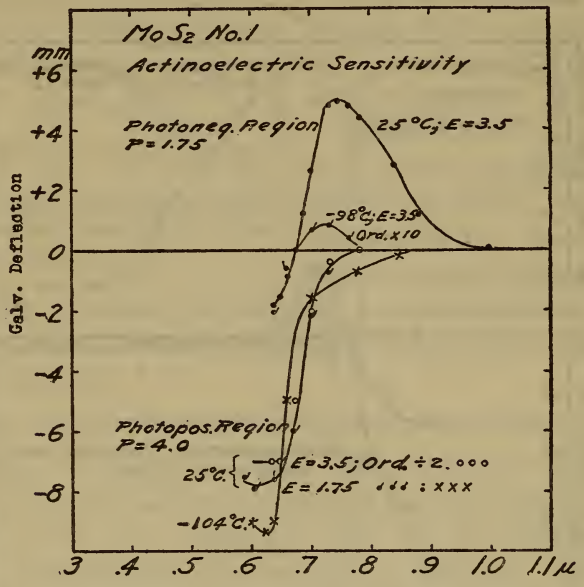

FIG. 22.—*Effect of temperature upon the spectroactinoelectric sensitivity of molybdenite. Sample No. 1*

VI. SUMMARY.

When molybdenite is heated by thermal conduction or exposed to thermal radiation it is found to possess thermoelectric, actinoelectric, and photoelectric properties, which, in varying degrees, are exhibited singly or collectively in a single crystal. The purpose of this paper is to describe some of these properties.

1. THERMOELECTRIC PROPERTIES.

The molybdenite investigated was in the form of thin cleavage pieces, some laminaa being 6 cm or more in length. To the ends were attached fine copper wires which formed the thermojunctions.

Previously published measurements gave a thermoelectric power of +750 microvolts (mv).

The present measurements, on samples from various sources, gave values of +690 mv down to +100 mv, through zero thermal emf to −1,040 mv.

In one sample, one end gave +510 mv and the other end gave −1,040 mv, against copper, at 28° C.

The latter is not unlike a compound thermoelectric series of copper-iron-bismuth-copper. Evidently molybdenite is not of sufficient homogeneity to specify its thermoelectrical properties.

2. ACTINOELECTRIC AND PHOTOELECTRIC EFFECTS.

The term *actinoelectric* is used to identify an *electromotive force* which may be manifested in a substance when exposed to thermal radiation, but without an impressed potential, in contradistinction to the *photoelectric change in resistance* which some substances undergo when subjected to an impressed emf and exposed to thermal radiation.

The actinoelectric phenomenon is more common than is the photoelectric effect; occurring in both the high and the low resistance class of molybdenite.

The intrinsic sensitivity of the actinoelectric reaction seems to be the highest in the low-resistance class of molybdenite, which is just the opposite of the photoelectric reaction.

Both effects are usually observed in small spots or loci in the lamina; and both phenomena may be found in the same lamina.

The actinoelectric emf of these spots, which are sometimes separated by only 0.5 to 1.5 mm, may be positive or negative. The polarity of this emf does not appear to have any relation with the positive and negative thermal emfs observed at the ends of the sample, connected with the copper electrodes.

The spectral actinoelectric effect may be positive or negative, depending upon the wave length of the thermal radiation stimulus, just as was previously observed for the photoelectrical effect.

The maximum of the spectral actinoelectric reaction is produced by thermal radiation stimuli of wave lengths between 0.65 and 0.9 μ There may be several such maxima in this spectral region. The material seems to be insensitive actinoelectrically to radiation stimuli of wave lengths greater than about 1 μ.

On the other hand, the maxima of the spectral photoelectric reaction in molybdenite usually occur beyond 0.8 μ; and the sensitivity extends to 2 μ. Moreover, the magnitude of the photoelectrical reaction may be from 75 to 100 times greater than the

actinoelectrical response. Hence, since the former is usually observed with an insensitive galvanometer the actinoelectrical reaction has no effect upon previously published data on the spectraphotoelectrical sensitivity of molybdenite.

The time for attaining the maximum spectral actinoelectric response is practically instantaneous irrespective of the kind (high or low resistance) of molybdenite examined, and of the wave length of the exciting radiation.

On the other hand, in the typical, high-resistance, high-photoelectrical sensitivity class of molybdenite, for certain wave lengths of the exciting radiation, the photoelectrical reaction requires from one to several minutes to attain a maximum, and twice that time for recovery after exposure to thermal radiation.

In the typical low-resistance, low-photoelectrical sensitivity but high-actinoelectrical sensitivity class of molybdenite, the spectraphotoelectrical reaction appears to be instantaneous irrespective of the wave length of the radiation stimulus.

Lowering the temperature shifts the maximum of the actinoelectrical reaction toward the short wave lengths; but this shift is much less than obtains in the photoelectric reaction.

Lowering the temperature has no marked effect upon the intrinsic actinoelectric sensitivity, as compared with the marked increase in photoelectrical sensitivity observed under similar conditions.

Increasing the intensity of the exciting radiation appears to produce a more rapid response on the short wave length side than on the long wave length side of the maximum of the spectral actinoelectric reaction, which is just the reverse of the previously observed, spectrophotoelectric reaction under similar conditions.

When there is a close coincidence of the spots or loci of actinoelectrical and photoelectrical sensitivity the photoelectric current is amplified or weakened, depending whether the external battery current flows with or against the actinoelectric current. As a result of this selective response, instead of obtaining the same photoelectrical reaction on reversal of the battery current, as usually observed, there is a difference, of 1.5 to 2.5 times, between the maximum and the minimum photoelectric effect.

From the data at hand it appears that the actinoelectric phenomenon is independent of other agencies that may be acting in molybdenite.

WASHINGTON, October 27, 1923.